phenol and β-chloroallyl alcohol was also investigated. Although pure hydroxy-ethers were not obtained, analytical data indicated that the reaction proceeded mainly in the expected manner.

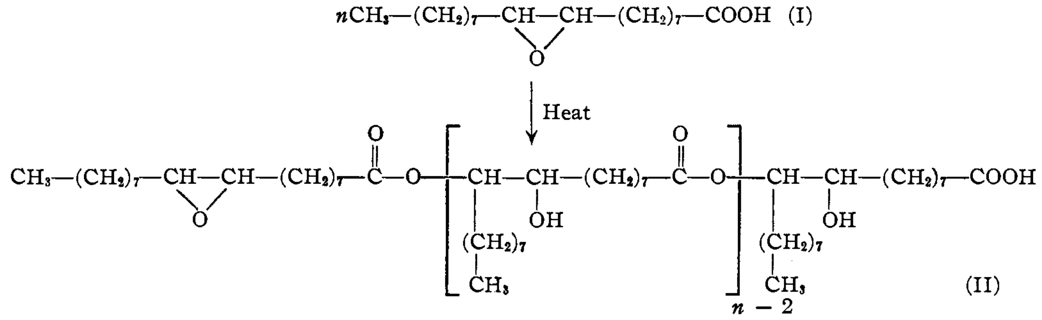
PHILADELPHIA 18, PA. RECEIVED JULY 10, 1947

[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Chemistry of Epoxy Compounds. VI.[2] Thermal Polymerization of the Isomeric 9,10-Epoxystearic Acids[1a]

BY DANIEL SWERN, GERALDINE N. BILLEN AND C. ROLAND EDDY

The isomeric 9,10-epoxystearic acids[3,4] (I), m. p. 59.5° and 55.5°, contain two very reactive functional groups, and theoretically they should yield linear polyesters of structure II on thermal polymerization at relatively low temperatures. (Mixtures of isomers would be obtained, since it is equally probable that the oxirane ring would be opened between the oxygen atom and C_9 or C_{10}).



$$n\mathrm{CH_3{-}(CH_2)_7{-}\underbrace{CH{-}CH}_{O}{-}(CH_2)_7{-}COOH}\quad\text{(I)}$$

$$\Big\downarrow\text{Heat}$$

$$\mathrm{CH_3{-}(CH_2)_7{-}\underbrace{CH{-}CH}_{O}{-}(CH_2)_7{-}\overset{O}{\overset{\|}{C}}{-}O}{-}\left[\mathrm{\underset{\underset{CH_3}{|}}{\underset{(CH_2)_7}{|}}{CH}{-}\underset{OH}{\underset{|}{CH}}{-}(CH_2)_7{-}\overset{O}{\overset{\|}{C}}{-}O}\right]_{n-2}{-}\mathrm{\underset{\underset{CH_3}{|}}{\underset{(CH_2)_7}{|}}{CH}{-}\underset{OH}{\underset{|}{CH}}{-}(CH_2)_7{-}COOH}\quad\text{(II)}$$

Since no product of reaction would be eliminated in their formation and since the molecular formula of the recurring unit would be identical with that of the monomer, they would resemble addition polymers, but on hydrolysis they would yield a monomer whose molecular formula is not identical with that of the recurring unit, and in this respect they would resemble condensation polymers.[5] This interesting point, coupled with the fact that convenient methods for the laboratory preparation of the isomeric 9,10-epoxystearic acids in a high degree of purity were available,[3,4] prompted us to study the quantitative thermal polymerization of these compounds.

A limited amount of work on the thermal polymerization of the 9,10-epoxystearic acids has been published,[6] but the starting materials were apparently impure and, in general, higher temperatures than necessary were employed, thereby encouraging side reactions.

Experimental

Starting Materials.—The isomeric 9,10-epoxystearic acids, m. p. 59.5° and 55.5°, were prepared from pure oleic and elaidic acids, respectively, by epoxidation with peracetic or perbenzoic acids.[3,4] *Anal.* Calcd. for $C_{18}H_{34}O_3$: neutralization equivalent, 298.5; oxirane oxygen,[6,7] 5.36. Found: neutralization equivalent, 297.5–299.5; oxirane oxygen, 5.32–5.37.

Polymerization Procedures.—Approximately 5-g. portions of the 9,10-epoxystearic acids were weighed into a series of test-tubes. The tubes were flushed with nitrogen, tightly stoppered and immersed in a constant temperature oil-bath which maintained the desired temperature to ±0.2°. Fifteen minutes was allowed for the establishment of temperature equilibrium before polymerization times were counted. At selected time intervals, a tube was removed from the oil-bath and rapidly cooled to room temperature. The required analytical information was usually obtained within twenty-four hours.

Analytical Procedures.—Acid numbers were determined by means of 0.1 *N* aqueous sodium hydroxide on 0.15–0.30 g. of sample dissolved in neutralized 95% ethanol, phenolphthalein being employed as indicator. Oxirane oxygen was determined by the modified method of Nicolet and Poulter.[6,7] Carbonyl oxygen analyses were conducted by the method described by Leithe,[8] except that a *p*H meter was employed to determine the end-point.

Discussion

The course of the polymerization of 9,10-epoxystearic acid, m. p. 59.5°, at 65°, 75° and 85° is shown in Tables I, II and III, and that of its isomer, m. p. 55.5°, at 75°, 100° and 120° is shown in Tables IV, V and VI. The rate of disappearance of the oxirane and carboxyl groups is plotted in

---

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

(1a) This paper was presented at the meeting-in-miniature of the Philadelphia section of the American Chemical Society held in Philadelphia, Pa., Jan. 22, 1948.

(2) For the previous paper in this series, see THIS JOURNAL, **70**, 1226 (1948).

(3) Swern, Findley and Scanlan, *ibid.*, **66**, 1925 (1944).

(4) Findley, Swern and Scanlan, *ibid.*, **67**, 412 (1945).

(5) Carothers, *ibid.*, **51**, 2548 (1929).

(6) Nicolet and Poulter *ibid.*, **52**, 1186 (1930).

(7) Swern, Findley, Billen and Scanlan, *Anal. Chem.*, **19**, 414 (1947).

(8) Leithe, *Fette u. Seifen*, **45**, 615 (1938).

TABLE I

THERMAL POLYMERIZATION AT 65° OF 9,10-EPOXYSTEARIC ACID, M. P. 59.5°

Time, hours	n^{60}_{D} (Abbe)	Acid no.	% Decrease in acid no.	% Oxirane oxygen	% Decrease in oxirane oxygen	Moles of carboxyl group per 100 g. of monomer[a]	Moles of oxirane group per 100 g. of monomer[b]	Physical appearance
0	1.4450	188.0	0	5.36	0	0.335	0.335	White solid
2	1.4459	181.5	3.46	5.10	4.85	.324	.319	White solid
4	1.4465	177.0	5.86	4.87	9.14	.316	.304	White solid
7	1.4474	170.2	9.46	4.57	14.7	.303	.286	White solid
24	1.4519	145.2	22.8	3.65	31.9	.259	.228	Partially solid
30	1.4530	137.0	27.1	3.51	34.5	.244	.219	Viscous oil
48	1.4555	122.2	35.0	2.75	48.7	.218	.172	Viscous oil
96	1.4590	97.0	48.4	2.06	61.6	.173	.129	Viscous oil
144	1.4610	82.0	56.4	1.52	71.7	.146	.095	Viscous oil
226	1.4629	70.5	62.5	0.89	83.4	.126	.056	Viscous oil
344	1.4639	59.8	68.2	0.47	91.2	.107	.029	Viscous oil
576	1.4650	51.2	72.8	0.10	98.2	.091	.006	Viscous oil

[a] Moles of carboxyl group per 100 g. of monomer = acid number/561.0. [b] Moles of oxirane group per 100 g. of monomer = % oxirane oxygen/16.

TABLE II

THERMAL POLYMERIZATION AT 75° OF 9,10-EPOXYSTEARIC ACID, M. P. 59.5°

Time, hours	n^{60}_{D} (Abbe)	Acid no.	% Decrease in acid no.	% Oxirane oxygen	% Decrease in oxirane oxygen	Moles of carboxyl group per 100 g. of monomer	Moles of oxirane group per 100 g. of monomer	Physical appearance
0	1.4450	188.0	0	5.37	0	0.335	0.336	White solid
2	1.4470	177.7	5.48	4.89	8.94	.317	.306	White solid
4	1.4480	168.4	10.4	4.55	15.3	.300	.284	White solid
8	1.4508	152.9	18.7	3.98	25.9	.273	.249	Partially solid
18	1.4549	128.5	31.7	3.09	42.5	.229	.193	Viscous oil
32	1.4576	103.9	44.7	2.25	58.1	.185	.141	Viscous oil
56	1.4601	84.7	54.8	1.63	69.6	.151	.102	Viscous oil
101	1.4625	66.6	64.6	1.04	80.8	.119	.065	Viscous oil
200	1.4651	52.3	72.2	0.65	87.9	.093	.041	Viscous oil
312	1.4660	46.1	75.6	0.22	95.9	.082	.014	Viscous oil
392	1.4662	...	..	..	..	...	...	Viscous oil[a]
504	....	...	..	..	..	...	...	Gel

[a] Viscous oil only partially soluble in ethyl alcohol, isopropyl alcohol and acetone.

TABLE III

THERMAL POLYMERIZATION AT 85° OF 9,10-EPOXYSTEARIC ACID, M. P. 59.5°

Time, hours	n^{60}_{D} (Abbe)	Acid no.	% Decrease in acid no.	% Oxirane oxygen	% Decrease in oxirane oxygen	Moles of carboxyl group per 100 g. of monomer	Moles of oxirane group per 100 g. of monomer	Physical appearance
0	1.4450	188.0	0	5.36	0	0.335	0.335	White solid
2	1.4491	163.6	13.0	4.48	16.4	.292	.280	White solid
4	1.4518	148.1	21.2	3.88	27.6	.264	.242	Partially solid
8	1.4543	128.4	31.7	3.18	40.6	.229	.199	Partially solid
16	1.4580	106.3	43.5	2.56	52.2	.190	.160	Viscous oil
32	1.4611	75.2	60.0	1.24	76.8	.134	.077	Viscous oil
64	1.4639	59.3	68.5	0.72	86.6	.105	.045	Viscous oil
128	1.4655	50.1	73.4	0.37	93.2	.089	.023	Viscous oil
256	....	...	..	..	..	...	...	Gel

Figs. 1 and 2 for the high-melting isomer and in Figs. 3 and 4 for the low-melting isomer.

Examination of the tables and figures reveals several significant points. First, both epoxy-acids may be polymerized to form gels. Second, in the polymerization of the high-melting isomer, m. p. 59.5°, the oxirane group disappears more rapidly than the carboxyl group throughout the reaction. In fact at the gel point more than 90% of the oxirane group has been consumed, whereas only about 73–76% of the carboxyl group has disappeared. Third, in the polymerization of the low-melting isomer, m. p. 55.5°, the rates of disappearance of both the oxirane and carboxyl groups are almost the same over the entire period investigated. This is best observed when Figs. 3

TABLE IV

THERMAL POLYMERIZATION AT 75° OF 9,10-EPOXYSTEARIC ACID, M. P. 55.5°

Time, hours	n^{60}D (Abbe)	Acid no.	% Decrease in acid no.	% Oxirane oxygen	% Decrease in oxirane oxygen	Moles of carboxyl group per 100 g. of monomer	Moles of oxirane group per 100 g. of monomer	Physical appearance
0	1.4419	189.0	0	5.35	0	0.337	0.334	White solid
4	1.4421	185.6	1.80	5.28	1.31	.331	.330	White solid
8	1.4422	182.8	3.28	5.19	2.99	.326	.324	White solid
16	1.4428	179.8	4.87	5.10	4.67	.321	.319	White solid
32	1.4434	173.6	8.14	4.92	8.04	.310	.307	White solid
64	1.4448	161.6	14.8	4.58	14.4	.287	.286	White solid
128	1.4488	139.5	26.2	3.84	28.2	.249	.244	White solid
256	1.4527	110.0	41.8	3.21	40.0	.196	.201	White solid
512	1.4569	74.9	60.4	2.29	59.2	.134	.143	Partially solid

TABLE V

THERMAL POLYMERIZATION AT 100° OF 9,10-EPOXYSTEARIC ACID, M. P. 55.5°

Time, hours	n^{60}D (Abbe)	Acid no.	% Decrease in acid no.	% Oxirane oxygen	% Decrease in oxirane oxygen	Moles of carboxyl group per 100 g. of monomer	Moles of oxirane group per 100 g. of monomer	Physical appearance
0	1.4419	187.3	0	5.32	0	0.334	0.332	White solid
4	1.4442	175.3	6.41	5.04	5.26	.313	.315	White solid
8	1.4458	165.0	11.9	4.76	10.5	.294	.297	Partially solid
16	1.4478	151.5	19.1	4.39	17.5	.270	.274	Partially solid
32	1.4510	123.9	33.9	3.33	37.4	.221	.208	Partially solid
64	1.4549	90.4	51.8	2.78	48.9	.161	.174	Viscous oil
128	1.4582	61.3	67.2	1.96	63.2	.109	.122	Viscous oil
256	1.4609	36.5	80.6	1.35	74.6	.065	.084	Viscous oil
512	1.4624	19.6	89.6	0.98	81.6	.035	.061	Viscous oil

TABLE VI

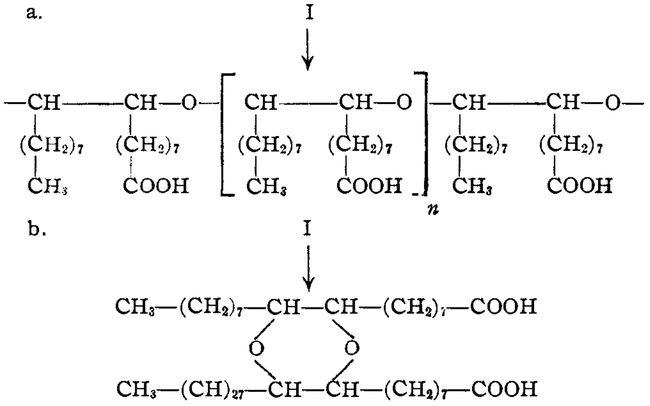
THERMAL POLYMERIZATION AT 120° OF 9,10-EPOXYSTEARIC ACID, M. P. 55.5°

Time, hours	n^{60}D (Abbe)	Acid no.	% Decrease in acid no.	% Oxirane oxygen	% Decrease in oxirane oxygen	Moles of carboxyl group per 100 g. of monomer	Moles of oxirane group per 100 g. of monomer	Physical appearance
0	1.4419	187.3	0	5.32	0	0.334	0.332	White solid
4	1.4480	149.4	20.2	4.33	18.6	.266	.271	Partially solid
8	1.4510	126.5	32.5	3.77	29.1	.226	.236	Partially solid
16	1.4545	95.8	48.9	2.87	46.1	.171	.179	Partially solid
32	1.4584	65.4	65.1	2.10	60.6	.117	.131	Viscous oil
64	1.4609	41.9	77.6	1.48	72.2	.075	.093	Viscous oil
128	1.4624	27.1	85.6	1.04	80.4	.048	.065	Viscous oil
256	1.4638	16.3	91.2	0.80	85.0	.029	.050	Viscous oil
512	....	...	..	..	..	...	...	Gel

and 4 are superimposed, although it is fairly evident from Tables IV, V and VI. Fourth, the polymerization of the high-melting isomer proceeds at a more rapid rate than that of the low-melting isomer.

The fact that both epoxy-acids may be polymerized to gels indicates that these compounds have a higher functionality than two. Consideration of the possible addition and condensation reactions which may occur makes this point evident. These reactions are listed below:

1. Reaction between the oxirane and carboxyl groups (addition reaction).
2. Reaction between the hydroxyl groups, formed as a result of reaction 1, and carboxyl groups, with the elimination of water (condensation reaction).



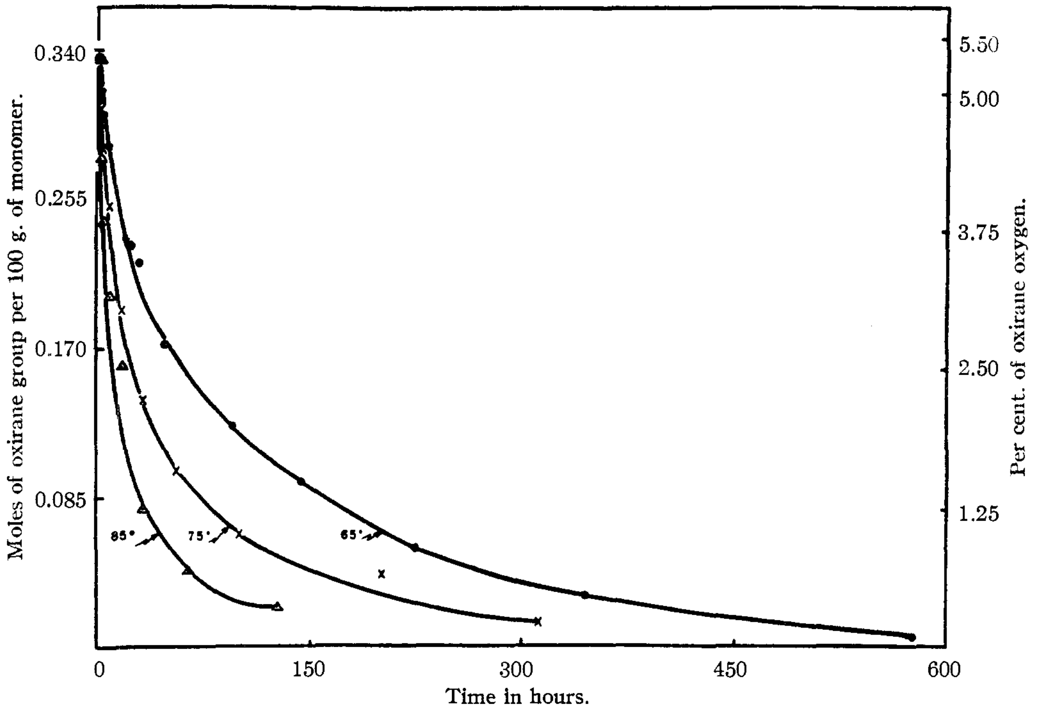


Fig. 1.—Thermal polymerization of 9,10-epoxystearic acid, m. p. 59.5°.

3. Reaction between the hydroxyl groups, formed as a result of reaction 1, and oxirane groups (addition reaction).

4. Reaction between oxirane groups (addition reactions).

5. Reaction between the hydroxyl groups, formed as a result of reaction 1, with the elimination of water (condensation reaction).

Reaction 1 is undoubtedly the main polymerization reaction, since carboxyl groups react readily with oxirane groups at moderate temperatures without catalysts, but such a reaction cannot ac-

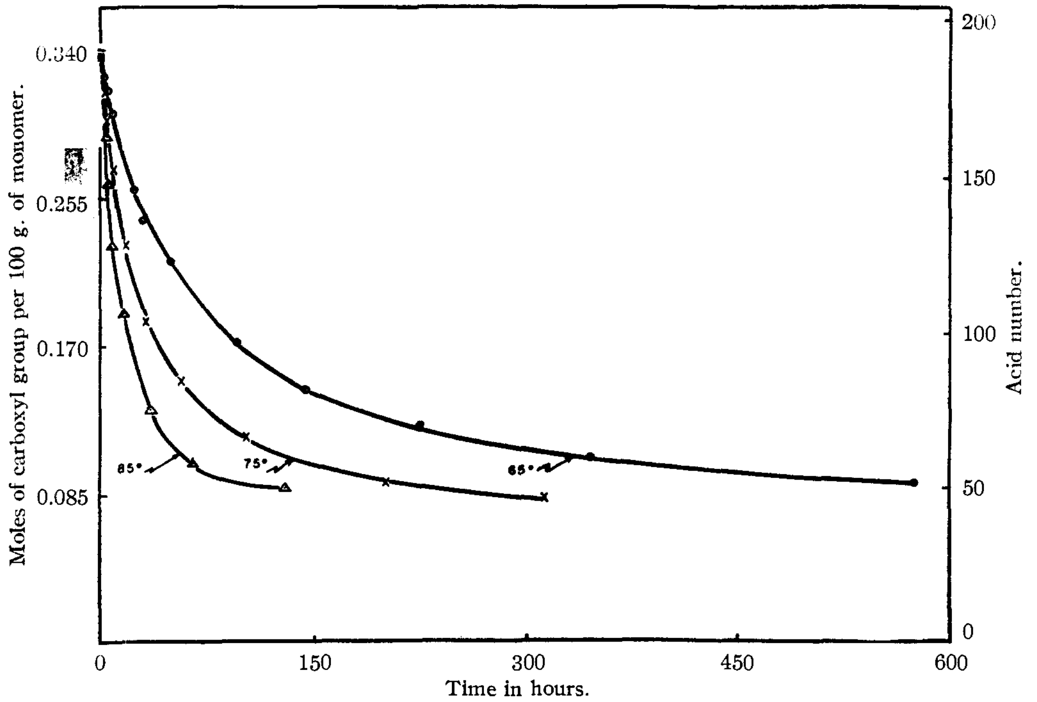


Fig. 2.—Thermal polymerization of 9,10-epoxystearic acid, m. p. 59.5°.

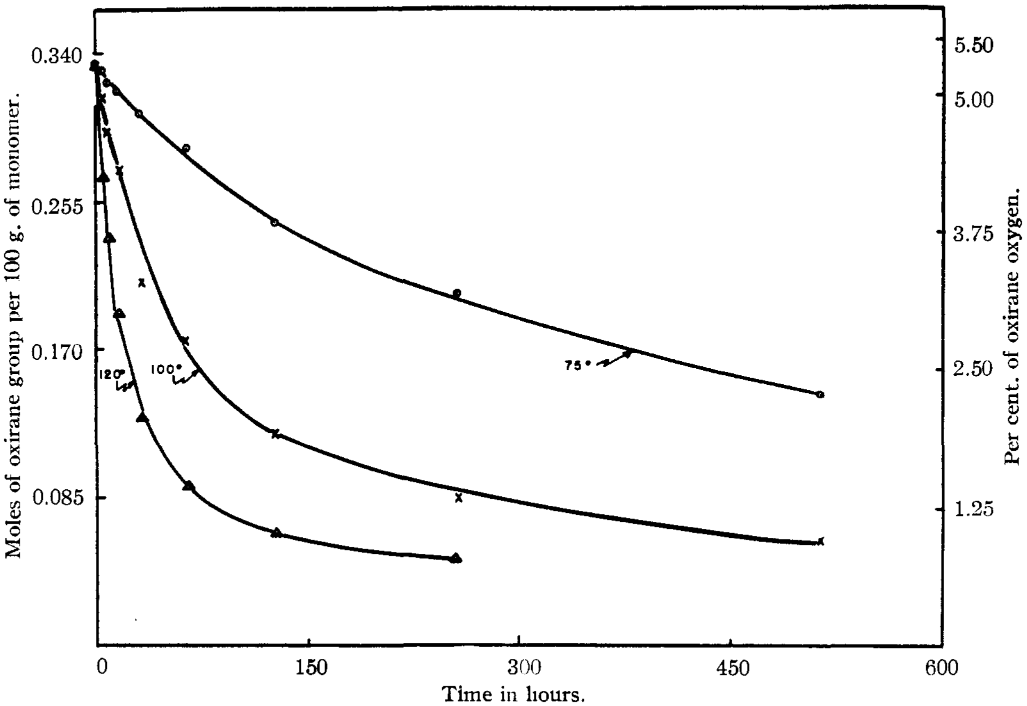


Fig. 3.—Thermal polymerization of 9,10-epoxystearic acid, m. p. 55.5°.

count for gel formation, since it yields only linear polyesters. Likewise, reaction 4b, which yields a difunctional dimer, cannot account for gel formation. The concept that reaction 4b may account for the oxirane group's disappearance at a more rapid rate than the carboxyl group's in the high-melting isomer, is not tenable because such a reaction requires high temperatures and acid catalysts. Reactions 2, 3 and 5, however, are cross-linking reactions, and reaction 4a yields a polyfunctional product capable of cross-linking. Reactions 4a and 5, however, in common with reac-

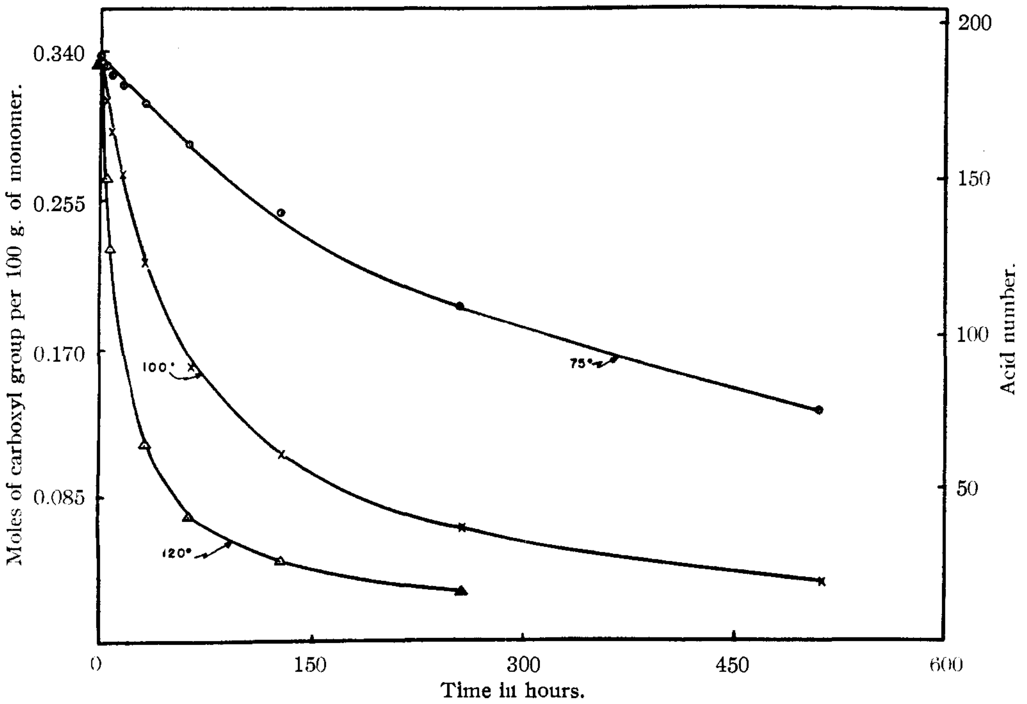


Fig. 4.—Thermal polymerization of 9,10-epoxystearic acid, m. p. 55.5°.

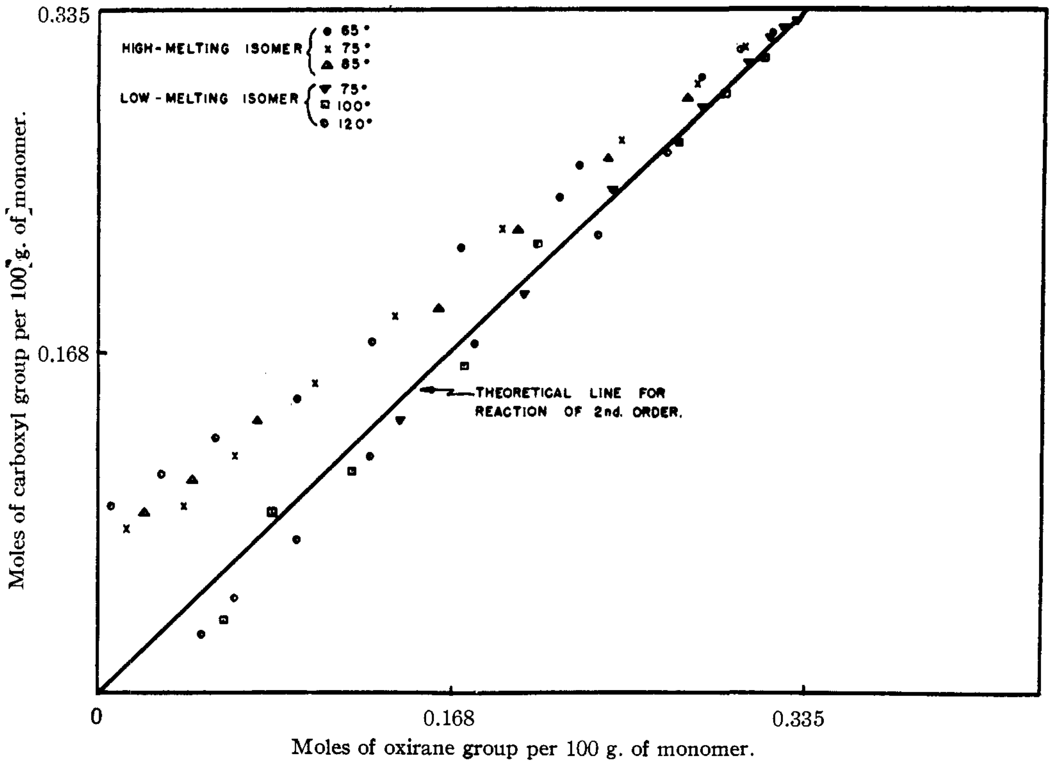


Fig. 5.—Thermal polymerization of the 9,10-epoxystearic acids, m. p. 59.5° and 55.5°.

tion 4b, require catalysts and high temperatures and probably do not account for cross-linking in either isomer or for the oxirane group's disappearance at a greater rate than the carboxyl group's in the high-melting isomer. Although we cannot state positively which of the remaining cross-linking reactions predominate, in the high-melting isomer it is probably reaction 3, and in the low-melting isomer it is probably reaction 2. These reactions can account not only for gelation, but reaction 3 also accounts for the oxirane group's disappearance at a more rapid rate than the carboxyl group's in the high-melting isomer, and reaction 2 accounts for the carboxyl group's disappearance at a slightly more rapid rate than the oxirane group's in the low-melting isomer, noticeable toward the end of the reaction. The assumption that reaction 3 accounts for gelation in the high-melting isomer is consistent with the fact that the oxirane group in this isomer reacts considerably faster with various simple secondary alcohols than the oxirane group in the low-melting isomer.

It was thought that the disappearance of the oxirane group at a more rapid rate than the disappearance of the carboxyl group in the high-melting isomer might be explained on the assumption that this group was isomerizing to the carbonyl group. Carbonyl oxygen analyses,[8] however, carried out on the polymers just prior to the gel point indicated that this reaction would account for only about one-third of the oxirane groups which had disappeared in excess of the carboxyl groups. In the low-melting isomer, carbonyl oxygen values were negligible, as would be expected from the data already discussed.

Cross-linking reactions must occur to only a limited extent in the low-melting 9,10-epoxystearic acid, since the disappearance of the carboxyl and oxirane groups proceeds at nearly the same rate throughout the entire polymerization and gelation does not occur until about 85% of the oxirane groups have disappeared. The parallel disappearance of these two functional groups suggested that the polymerization of this isomer might be a simple second order reaction. In Fig. 5, the concentration of carboxyl group is plotted against the concentration of oxirane group both for this isomer and the high-melting one. If the only process is a second order reaction between oxirane and carboxyl groups, a straight line which makes an angle of 45° with the co-ordinate axes, should be obtained. In the low-melting isomer, the points fall almost exactly on this line during the early stages of the polymerization, and diverge slightly toward the later stages. The best straight line drawn through these points makes an angle of 47° with the abscissa. It was fairly obvious from an inspection of the data in Tables I, II and III and by superimposition of Figs. 1 and 2, that a simple second order reaction was not the sole process occurring in the high-melting isomer, but this fact was strikingly illustrated when the points for this isomer, m. p. 59.5°, were also plotted in Fig. 5.

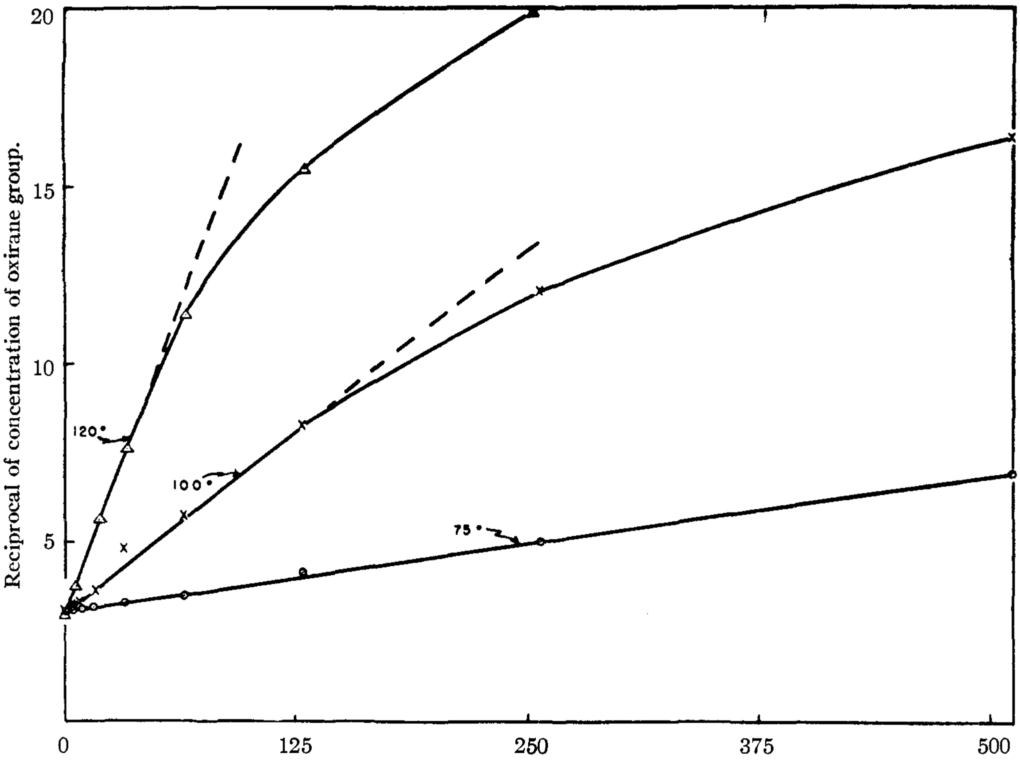


Fig. 6.—Thermal polymerization of 9,10-epoxystearic acid, m. p. 55.5°.

These points diverge from the line for equimolar disappearance of the oxirane and carboxyl groups even during the early stages of the reaction, and the best straight line drawn through these points makes an angle of about 36° with the abscissa.

Furthermore, if the second order reaction between oxirane and carboxyl groups is the only process occurring, plotting the reciprocal of the concentration of either the oxirane or carboxyl group against time should give a straight line, since both groups are initially present in equimolar amounts, and the slope of the line is the reaction rate constant, k. This is shown in Fig. 6 for the low-melting isomer only. At 75°, an almost perfect straight line is obtained over the entire range investigated, whereas at 100° and 120°, the first seven and five points, respectively, appear to fall on straight lines. These early points were replotted on larger graph paper, and the broken lines in Fig. 6 represent the extensions of the best straight lines for these points, as obtained from the plots on the larger graph paper. The rate constants at 75, 100 and 120° for the low-melting isomer are 0.00781, 0.0412 and 0.161, respectively (time in hours, concentration in moles per 100 g.). The energy of activation was calculated from the slope of the line in Fig. 7, in which log k is plotted against $1/T$. The value of E thus obtained is 18,600 calories per mole. The equation for correlating k with T is shown below

$$\log k = -4081/T + 9.59$$

Just prior to the gel point, the polymers are highly viscous, colorless oils, which are soluble in ethanol, diethyl ether, butanol, acetone, xylene, ethylene dichloride and ethyl acetate, and insoluble in water and in aliphatic hydrocarbons. At the gel stage, the polymers are insoluble in all these solvents at their boiling points.

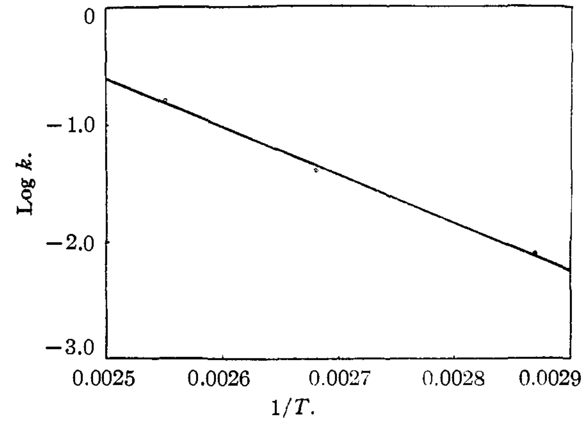


Fig. 7.—Thermal polymerization of 9,10-epoxystearic acid, m. p. 55.5°.

Acknowledgment.—We are indebted to Rudolph Speiser, Thomas W. Findley and John T. Scanlan for valuable discussions in connection with this problem.

Summary

The thermal polymerization of the isomeric 9,10-epoxystearic acids, m. p. 59.5° and 55.5°, derivable from oleic and elaidic acids, respectively, has been quantitatively studied. Both isomers can be polymerized to the gel stage, the high-melting isomer yielding a gel when about 75% of the carboxyl groups and 95% of the oxirane groups have disappeared, the low-melting isomer when about 85% of the oxirane groups and 90% of the carboxyl groups have disappeared. The main process appears to be the formation of linear polyesters by the reaction of the oxirane with the carboxyl group.

In the high-melting isomer, side reactions, which take place from the beginning of the reaction, cause the oxirane group to disappear at a more rapid rate than the carboxyl group, thereby preventing a kinetic analysis of the polymerization. In the low-melting isomer, the approximately parallel disappearance of both functional groups permits calculation of reaction rate constants as well as activation energy. This latter value is 18,600 cal. per mole. For both isomers, the reaction rate approximately doubles for each ten-degree rise in temperature.

The polymers just prior to the gel stage are highly viscous, colorless oils, soluble in many common organic solvents, and insoluble in water and in aliphatic hydrocarbons. At the gel stage they are insoluble at the boiling point in all the solvents tested.

PHILADELPHIA 18, PA. RECEIVED JULY 10, 1947

[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Chemistry of Epoxy Compounds. VII.[2] Stereochemical Relationships between the 9,10-Epoxy-, Chlorohydroxy- and Dihydroxystearic Acids

BY DANIEL SWERN

The stereochemical relationships involved in the conversion of oleic and elaidic acids (*cis*- and *trans*-9-octadecenoic acids, respectively) to the 9,10-dihydroxystearic acids by way of the intermediate oxirane and chlorohydroxy compounds have been studied by King[3] and also by Atherton and Hilditch.[4] These investigators have proposed reaction schemes which not only differ on several fundamental points but which are at variance with accepted thinking on the Walden inversion[5] and double bond addition reactions[5] in some important respects.

A satisfactory reaction scheme must be in agreement with the following experimentally determined facts: (1) The 9,10-epoxystearic acid obtained from oleic acid by epoxidation with organic per-acids and that obtained by hypohalogenation and subsequent dehydrohalogenation are identical, and therefore have the same configuration; (2) the 9,10-epoxystearic acid obtained from elaidic acid by epoxidation and that obtained by hypohalogenation and dehydrohalogenation are also identical, and differ from the 9,10-epoxystearic acid described under (1) above; (3) the 9,10-dihydroxystearic acid obtained from oleic acid by oxidation with potassium permanganate and that obtained from elaidic acid by epoxidation and subsequent hydrolysis are identical; (4) the 9,10-dihydroxystearic acid obtained from elaidic acid by oxidation with potassium permanganate and that obtained from oleic acid by epoxidation and hydrolysis are also identical and differ from the 9,10-dihydroxystearic acid described under (3) above; (5) the chlorohydroxystearic acids obtained from oleic acid by reaction with hypochlorous acid and those obtained by epoxidation of oleic acid and subsequent treatment of the 9,10-epoxystearic acid with hydrochloric acid are identical; (6) the chlorohydroxystearic acids obtained from elaidic acid by reaction with hypochlorous acid and those obtained by epoxidation of elaidic acid and treatment of the 9,10-epoxystearic acid with hydrochloric acid are also identical and differ from the chlorohydroxystearic acids described under (5) above; and (7) treatment of either 9,10-dihydroxystearic acid with hydrochloric acid, followed by dehydrohalogenation and hydrolysis, yields the other isomer.

For some time we have been studying the reactions discussed above, and in this paper we are suggesting a scheme which correlates configurational relationships involved, in harmony with accepted theories of the Walden inversion and double bond addition reactions. This reaction scheme is shown in Fig. 1 (the + and − signs do not refer to optical rotations but are employed to correlate configurational relationships and to demonstrate the inversions more clearly).

Although it is generally agreed that opening and closing of the oxirane ring is accompanied by inversion,[6,7,8,9] and this rule has been followed in re-

---

[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

[2] For paper VI of this series, see THIS JOURNAL, **70**, 1228 (1948).

[3] King, *J. Chem. Soc.*, 387 (1942).

[4] Atherton and Hilditch, *ibid.*, 204 (1943).

[5] Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940; Remick, "Electronic Interpretations of Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1943.

[6] Kuhn and Ebel, *Ber.*, **58**, 919 (1925).

[7] Böeseken and co-workers, *Rec. trav. chim.*, **47**, 683 (1928). Consult this paper for previous contributions.

[8] Esafov, *J. Gen. Chem.* (*U. S. S. R.*), **7**, 1403 (1937).

[9] Wilson and Lucas, THIS JOURNAL, **58**, 2396 (1936); Winstein and Lucas, *ibid.*, **61**, 1576, 1581 (1939); Lucas, Schlatter and Jones, *ibid.*, **63**, 22 (1941); Wilson and Gould, *ibid.*, **63**, 2541 (1941).